

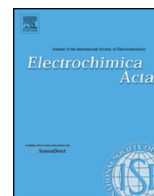


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Comparative Study of Basal-Plane Pyrolytic Graphite, Boron-Doped Diamond, and Amorphous Carbon Nitride Electrodes for the Voltammetric Determination of Furosemide in Pharmaceutical and Urine Samples

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ABSTRACT

Sensitive and simple electroanalytical methods were developed for the determination of the loop diuretic furosemide (FUR) in pharmaceutical formulations and synthetic urine samples by coupling square-wave voltammetry (SWV) with polished basal-plane pyrolytic graphite (BPPG) or cathodically pretreated boron-doped diamond (BDD) and amorphous carbon nitride (a-CN_x) as working electrodes. The analytical parameters obtained with the three methods were compared. With BPPG, best results were attained using 0.10 mol L⁻¹ H₂SO₄ as supporting electrolyte, whereas with BDD and a-CN_x, this was attained using a 0.040 mol L⁻¹ BR buffer (pH 4.5). Cyclic voltammograms obtained for FUR evidenced an irreversible behavior (with two oxidation peaks), in agreement with the literature. On the BDD and a-CN_x electrodes, the electrooxidation of FUR is a purely diffusion-controlled process, whereas on the BPPG electrode some degree of adsorption is also involved. The obtained linear response ranges (detection limits) for the BPPG, BDD, and a-CN_x electrodes were 0.60–4.8 (0.47), 0.30–13 (0.30), and 0.50–99 (0.39) μmol L⁻¹, respectively. The proposed methods were successfully applied in the determination of FUR in pharmaceutical formulations (tablets), with results similar to those obtained using a reference spectrophotometric method (at a confidence level of 95%), and in the recovery of FUR in synthetic urine samples. The analytical conditions obtained with the novel SWV methods here reported are comparatively better than those for other electrochemical methods in the literature. As the pretreatment procedures are much simpler for BDD and a-CN_x than for BPPG, one can conclude that the former two materials can be advantageously used to determine FUR with good sensitivity and selectivity.

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1. Introduction

For several reasons, analytical methods for the determination of furosemide are of significant interest. Furosemide (FUR), 4-chloro-2-[(2-furylmethyl) amino]-5-sulfamoylbenzoic acid (see Fig. 1), is a loop diuretic widely used for the treatment of edematous conditions and in the management of hypertension and other conditions for which the increase in urinary flow can relieve symptoms [1,2]. FUR has the function of blocking the absorption of

salt and fluid in the kidney tubules, causing a considerable increase in urine output. The diuretic effect of FUR can cause body water and electrolyte depletion; e.g. hypokalemia (deficiency of potassium in the blood stream), which can lead to symptoms such as cardiac dysrhythmia [1]. Thus, accurate medical supervision is necessary during treatment with FUR. Furthermore, diuretics abuse occurs quite commonly, e.g. by persons with eating disorders and athletes [1]; due to the latter case, FUR and several other diuretics are in the list of prohibited substances for athletes, published by the World Anti-Doping Agency [3]. Hence, rapid, simple, and sensitive methods for FUR determination in both pharmaceutical preparations and biological fluids are required.

Some years ago, Bosch et al. [4] reviewed the analytical determination of FUR. Often this determination is performed by

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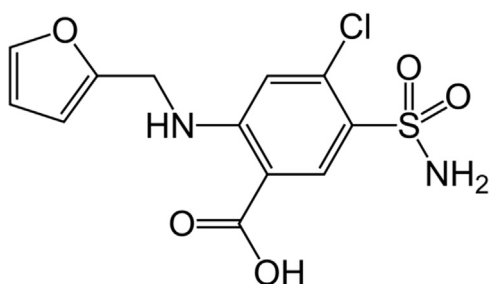


Fig. 1. Chemical structure of the furosemide molecule.

liquid chromatography, commonly with spectrophotometric [5,6,7], spectrofluorimetric [8], chemiluminescent [9], or mass-spectrometric [10,11] detection. However, in general these procedures involve some extraction and the use of toxic solvents and expensive devices; furthermore, often they are time-consuming. Some electrochemical procedures have also been developed [12–17]; when compared to other types of procedures, they generally present good sensitivity, with the advantage of being relatively inexpensive and rapid. In 1995, Barroso et al. [12] reported on the use of a glassy carbon (GC) electrode and the differential pulse (DPV) and square-wave voltammetry (SWV) techniques to determine piretanide and FUR in pharmaceuticals and spiked urine samples. Years later, Semaan et al. [13] developed a procedure for FUR determination in pharmaceuticals using a graphite-polyurethane composite electrode; cyclic voltammetry (CV), DPV, and SWV were used to quantify FUR, with best results being obtained by DPV. Baranowska et al. [14] reported on the determination of FUR simultaneously with paracetamol in spiked human urine (with prior extraction) using a graphite electrode and a DPV method. Next, a procedure using a gold electrode for the determination of FUR in pharmaceutical formulations by DPV was reported by Shetti et al. [15]. Then, Malode et al. [16] reported on the use of a multi-walled carbon nanotubes paste electrode for the voltammetric (DPV) determination of FUR in pharmaceutical formulations and urine. More recently, Hasanzadeh et al. [17] reported on the development of a DPV procedure for FUR determination in spiked human serum and urine fluids using a magnetic graphene oxide functionalized by chlorosulfonic acid-modified GC electrode.

For many years, several kinds of carbon materials have been extensively used as working electrodes in electroanalysis. As highlighted by McCreery [18], commonly cited advantages of these materials include low cost, wide potential window, relatively inert electrochemistry, and electrocatalytic activity for a variety of redox reactions. Graphite and GC are the carbon materials more often and extensively used as electrodes. They are used solely or combined with other materials, resulting in modified electrodes that generally present greater selectivity.

Pyrolytic graphite (PG) is a polycrystalline form of carbon that has a high degree of orientation and comprises both edge-plane (EPPG) and basal-plane pyrolytic graphite (BPPG). Until recently, it was thought that their chemical and electrochemical reactivity differed greatly [18–20], but more recently it has been reported that they can be similar [21]. For many years now, PG has been used as electrode material and as support for the development of modified electrodes, with good performance and some advantages (see e.g. [19,20,22–25]).

In the last 15 years, boron- or nitrogen-doped diamond (BDD or NDD) and diamond-like carbons (DLCs) have been extensively investigated as electrode materials for different electroanalytical procedures (see e.g. [26–32]). In fact, BDD films emerged as excellent electrode materials for several electrochemical applications, especially electrolytic (see e.g. ref. [33]) and electroanalytical ones (see e.g. ref. [29]). We have reported on the use of this

electrode as a substrate for biosensor development or directly for the electroanalytical determination of several analytes (singly or simultaneously), such as additives in food products and drugs in pharmaceutical formulations (see e.g. [30,34–38]).

Amorphous carbon nitride (a-CN_x) films are a new class of advanced carbon material that present several properties similar to those of BDD, i.e. large potential window in aqueous solvents of 3.0–3.5 V [39], low double-layer capacitance values [40], and good electrochemical reactivity, which is dependent on their surface termination [41]. Similarly to BDD films, several factors may affect the properties of a-CN_x films, such as synthesis process, concentration of heteroatoms, and nature of surface terminations, which may be significantly modified by plasma or electrochemical pretreatments. For instance, more efficient charge transfer for the [Fe(CN)₆]⁴⁻/[Fe(CN)₆]³⁻ redox pair and better resolved peaks for the simultaneous detection and determination of dopamine and ascorbic acid have been reported after proper electrochemical pretreatment of a-CN_x electrodes [30,38,41–43]. In the case of BDD electrodes, their electrochemical activity for a given analyte may also be highly dependent on surface termination, i.e., whether they are hydrogen or oxygen terminated [44]. For instance, lower electroanalytical detection limits for different organic analytes have been attained after cathodic pretreatments, by which hydrogen terminations are increased on the BDD surface (see e.g. [36,37,45,46]).

As noted above, FUR has been electroanalytically determined using different kinds of electrode materials, including gold, GC, graphite-polyurethane composite, and multi-walled carbon nanotubes paste. In the present study, we report on the development of SWV procedures for FUR determination using non-modified carbon materials as electrodes, i.e. BPPG, BDD, and a-CN_x. The analytical conditions obtained with these electrodes are compared with respect to adsorption or not of oxidation products, linear range, sensitivity, detection limit etc. Finally, the respective analytical methods are applied in the determination of FUR in pharmaceutical formulations and synthetic urine samples; in the first application, the obtained results are compared with those attained with a spectrophotometric reference procedure.

2. Experimental

2.1. Apparatus

A BPPG disk (Graphtek L.L.C., USA), with a geometric area of 0.20 cm², was mounted in Teflon[®]. The a-CN_x films were homemade (prepared at LISE); their deposition conditions are described elsewhere [30]. The a-CN_x electrode was cut from a compact and pinhole-free film (about 400 nm thick), with atomic composition C_{0.84}N_{0.16}, deposited on a 1 cm × 5 cm, 0.3 mm thick foil of stainless steel (AISI 316L). The BDD films (NeoCoat, Switzerland), with specified 8000 ppm boron content, were prepared by the hot-filament chemical vapor deposition technique on a monocrystalline silicon (p-doped) substrate. A 10 mL three-electrode electrochemical cell was used, with a Pt wire as auxiliary electrode and an Ag/AgCl (3.0 mol L⁻¹ KCl) reference electrode; hereinafter all potentials are referred to this reference electrode. The exposed (geometric) area of the a-CN_x or BDD working electrode was 0.35 or 0.25 cm², respectively.

The CV and SWV experiments were performed using an Autolab PGSTAT-30 (Ecochemie) potentiostat/galvanostat, controlled with the GPES 4.9 software. The SW voltammograms were baseline-corrected by the moving average method (peak width: 0.003).

2.2. Reagents, supporting electrolytes, and standards

All reagents were of analytical grade. FUR was purchased from Sigma. An aqueous 0.04 mol L⁻¹ Britton-Robinson (BR) buffer

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